AMENDED SPECIFICATION

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PATENT SPECIFICATION

Application Date: Sept. 7, 1943. *No. 14624/43.*
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Complete Specification Accepted: Jan. 10, 1945.
Jan 10. 1945

PROVISIONAL SPECIFICATION

Improvements in or relating to the Silvering of Non-Metallic Surfaces

We, JOHNSON, MATTHEY & COMPANY, LIMITED, a British Company, ERNEST ROBERT BOX and ERIC JOHN WYETH, both British Subjects, all of 78, Hatton Garden, London, E.C.1, do hereby declare the nature of this invention to be as follows:—

This invention relates to a process for providing the surface of non-metallic articles as, for example, glass, mica, porcelain, earthenware or electrical insulating materials with a fired-on coating of precious metal which can act as a basis for soldering or electroplating, or can be used as an electrical resistor or conductor. The process can also be used in the production of designs or decorative effects in precious metal on the surface of non-metallic articles.

Methods of providing fired-on metallic coatings on non-metallic surfaces have long been known. For example such coatings may be obtained by painting, spraying or printing the non-metallic article with so-called "liquid metals" which consist of solutions of resinates or sulpho-resinates in various essential oils. They have also been obtained by painting, printing or spraying the surface with a paste of silver oxide or carbonate and a lead borate flux in an oil, glycerine or other combustible viscous medium. In both these processes the article is subsequently fired at a temperature sufficient to burn off the organic matter and leave a residual film of metal on the surface of the non-metallic article. Films produced from liquid metals are extremely thin and several coatings are required to produce a satisfactory film for use as a basis for soldering or as an electrical conducting layer. Films produced by the use of silver oxide or carbonate are much thicker but two or more applications of silvering paste are frequently necessary to obtain a sufficiently thick coating for many purposes. When the films of silvering paste are applied by a printing process they are frequently porous due to the contraction which occurs when the silver oxide or carbonate is converted into metallic silver during the firing-on process.

We have now found that dense, relatively non-porous adherent films of silver, gold or platinum may be obtained on non-metallic surfaces by applying to the surface a paste consisting of very finely divided metallic silver, gold or platinum and a fusible flux suspended in a combustible organic medium and then firing the article at a temperature at which the organic matter burns off and the flux softens sufficiently to cause the metal powder to adhere firmly to the non-metallic surface. Suitable fluxes are lead or bismuth borosilicates to which may be added an alkali silicate or borosilicate. Silver, gold and platinum are malleable metals and hence cannot be produced in a finely powdered form by grinding. Fine powders can however readily be obtained by treating solutions of salts of these metals or precipitated compounds of the metals with a reducing agent which may be a metal powder or an organic or inorganic reducing agent. Zinc powder is an example of a metal reducing agent, formaldehyde an example of an organic reducing agent and a soluble hypophosphite an example of an inorganic reducing agent, but the invention is not restricted to the use of any of these reducing agents since any other such agent which produces the metals in a finely divided form is suitable. The

[*Price* 1/-]

reduced metal powder is washed free from salts, dried at a low temperature to prevent agglomeration of the particles and then ground with the flux and a suitable medium for spraying, painting or printing. For spraying the medium may consist of a solution of cellulose nitrate in amyl acetate.

A suitable medium for painting consists of a solution of resin in pure turpentine.

When the paste is required for printing the medium may be any of the usual oils used in making printers inks or lithographic inks or it may consist of a solution of cellulose nitrate in butyl lactate.

Dated this 7th day of September, 1943.
J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields,
London, W.C.2,
Chartered Patent Agents.

COMPLETE SPECIFICATION

Improvements in or relating to the Silvering of Non-Metallic Surfaces

We, JOHNSON, MATTHEY & COMPANY, LIMITED, a British Company, ERNEST ROBERT BOX and ERIC JOHN WYETH, both British Subjects, all of 78, Hatton Garden, London, E.C.1, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to a process for providing the surface of non-metallic articles, as for example glass, mica, porcelain, earthenware or electrical insulating materials, with a fired-on coating of silver which can act as a basis for soldering or electroplating, or can be used as an electrical resistor or conductor. The process can also be used in the production of designs or decorative effects in silver on the surface of non-metallic articles.

Methods of providing fired-on metallic coatings on non-metallic surfaces have long been known. For example such coatings may be obtained by painting, spraying or printing the non-metallic article with so-called "liquid metals" which consist of solutions of resinates or sulphoresinates of the metals in various essential oils. They have also been obtained by painting, printing or spraying the surface with a paste of silver oxide or carbonate and a lead borate flux in an oil, glycerin or other combustible viscous medium. In both these known methods the article is subsequently fired at a temperature sufficient to burn off the organic matter and leave a residual film of metal on the surface of the non-metallic article. Films produced from "liquid metals" are extremely thin and several coatings are required to produce a film satisfactory for use as a basis for soldering or as an electrical conducting layer. Films produced by the use of silver oxide or carbonate are much thicker, but two or more applications of silvering paste are frequently necessary to obtain a sufficiently thick coating for many purposes. When the films of silvering paste are applied by a printing process they are frequently porous due to the contraction which occurs when the silver oxide or carbonate is converted into metallic silver during the firing-on process.

We have now found that dense, relatively non-porous adherent films of silver are obtained on non-metallic surfaces by applying to the surface by painting, spraying or printing a paste consisting of very finely divided metallic silver and a fusible flux comprising essentially lead or bismuth borosilicates in a combustible organic medium and then firing the coated article at a temperature at which the organic matter burns off and the flux softens sufficiently to cause the silver powder to adhere firmly to the non-metallic surface. An alkali silicate or borosilicate may be incorporated in the flux.

Silver is a malleable metal and hence cannot be produced in a finely powdered form by grinding. A fine powder can, however, readily be obtained by treating solutions of silver salts, or preferably precipitated silver compounds, for example the oxide, carbonate or oxalate, with a reducing agent which may be a metal powder or an organic or inorganic reducing agent. Zinc powder is an example of a metal reducing agent; formaldehyde and formic acid and alkaline tartrate or citrate solutions are examples of organic reducing agents; and soluble hypophosphites or hydrosulphites, titanous salts and alkaline hydrogen peroxide solutions are examples

of inorganic reducing agents, but the invention is not restricted to the use of any of these reducing agents since any other such agent which will produce the silver in a finely divided form is suitable. The reduced silver powder is washed free from salts and either dried at a low temperature to prevent agglomeration of the particles and then ground with the flux and a suitable medium for spraying, painting or printing, or ground wet with the flux, dried and then milled with the medium.

For spraying, the medium may consist of a solution, for example a 2½% solution, of cellulose nitrate in amyl acetate.

A suitable medium for painting consists of a solution, for example a 20% solution, of colophony or other resin in pure turpentine.

When the paste is required for printing, the medium may be any of the usual oils used in making printers inks or lithographic inks.

When the paste is required for silk screen printing, the medium may consist of a solution, for example a 10% solution, of cellulose nitrate in amyl lactate.

In any of these uses, varying amounts of pine oil may be added to retard the rate of drying.

The following Examples describe methods of obtaining pastes containing silver in a finely divided form, but the invention is not limited to these Examples.

EXAMPLE 1.

A solution of silver nitrate is treated with an excess of caustic soda solution to obtain a precipitate of silver oxide which is then washed free from soluble salts by decantation with hot water. The resulting slurry of silver oxide is treated with an excess of formaldehyde with vigorous stirring and heated until all the oxide is reduced to finely divided grey metallic silver. This powder is washed by decantation free from soluble substances, collected on the filter and dried in a steam oven. It is then mixed with 5 to 10% of finely ground lead borosilicate flux and the mixture is ground with a 10% solution of cellulose nitrate in a 2:1 mixture of amyl lactate and pine oil to form a paste for printing by the silk screen process.

EXAMPLE 2.

A solution of silver nitrate is treated with an excess of hot sodium carbonate solution and the resulting precipitate of silver carbonate is washed free from soluble salts by decantation with hot water. The slurry of silver carbonate is then reduced to metallic silver by boiling with an excess of sodium hydrosulphite ($Na_2S_2O_4$). After washing free from soluble salts, the silver powder is dried, mixed with the flux and medium as described in Example 1.

EXAMPLE 3.

A solution of silver nitrate is treated with hydrochloric acid until all the silver is precipitated as chloride. The acid is then removed by washing by decantation and the suspension of silver chloride is treated with 10% sulphuric acid and pure zinc powder until all the chloride has been reduced to metallic silver. Any excess of zinc is removed by adding more sulphuric acid and the resulting silver powder dried as in Example 1.

The silver powder produced may be ground with from 2½ to 10% of lead borosilicate flux and a 20% solution of colophony in a 1:1 mixture of pure turpentine and pine oil to produce a silver paste suitable for painting on the non-metallic bodies to produce, after firing, a conducting layer of silver which may serve as a basis for plating or soldering operations.

Silver layers may be produced on flat surfaces by means of the silk screen process using a paste produced by the process described in Example 1. In the silk screen process the paste is forced by means of a roller or squeegee through a silk screen onto the surface. The usual firing temperature for the paste is from 550° to 700° C., according to the material to which the paste is applied. If thick coatings of silver are required, it may be necessary to apply the paste two or more times with intermediate firings.

In Specification No. 569,388 which, although of earlier date, was not published at the date of the present application, there is claimed a process for the manufacture of an adherent film of finely comminuted silver upon a non-metallic surface by precipitating silver in the presence of a protective colloid, mixing the precipitant with other constituents to form a paste, applying said paste to the said surface, and applying heat to drive off the non-silver constituents. The silver obtained when precipitation is carried out in the presence of a protective colloid is, however, in an extremely fine state of subdivision. For the purposes of the present invention it has been found that the best results are obtained with the coarser form of precipitated metallic silver which is produced when no protective colloid is present.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we

claim is:—

1. A process of silvering a non-metallic article which consists in applying to the article by painting, spraying or printing a paste consisting of finely divided metallic silver and a fusible flux comprising essentially lead or bismuth borosilicates in a combustible organic medium, and firing the coated article to burn away the organic matter and leave a firmly adherent silver layer.

2. A process as claimed in claim 1 in which the finely divided metallic silver is prepared by wet reduction of a precipitated silver compound by means of a metallic, inorganic, or organic reducing agent.

3. A process as claimed in claim 1 or 2 in which the said paste is prepared by grinding precipitated metallic silver with the flux in an organic painting spraying or printing medium.

4. A process as claimed in claim 3 in which the spraying medium consists of a solution of cellulose nitrate in amyl acetate.

5. A process as claimed in claim 3 in which the silk screen printing medium consists of a solution of cellulose nitrate in amyl lactate.

6. A process as claimed in claim 3 in which the painting medium consists of a solution of colophony in pure turpentine.

7. A process according to any of claims 3 to 6 in which pine oil is added to the medium to retard the rate of drying.

8. For use in the process as claimed in any of claims 1 to 7, finely divided metallic silver or pastes containing the same when prepared by the method described in any of the foregoing Examples.

9. Silvered non-metallic articles when obtained by the process claimed in any of claims 1 to 7.

Dated this 16th day of August, 1944.

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